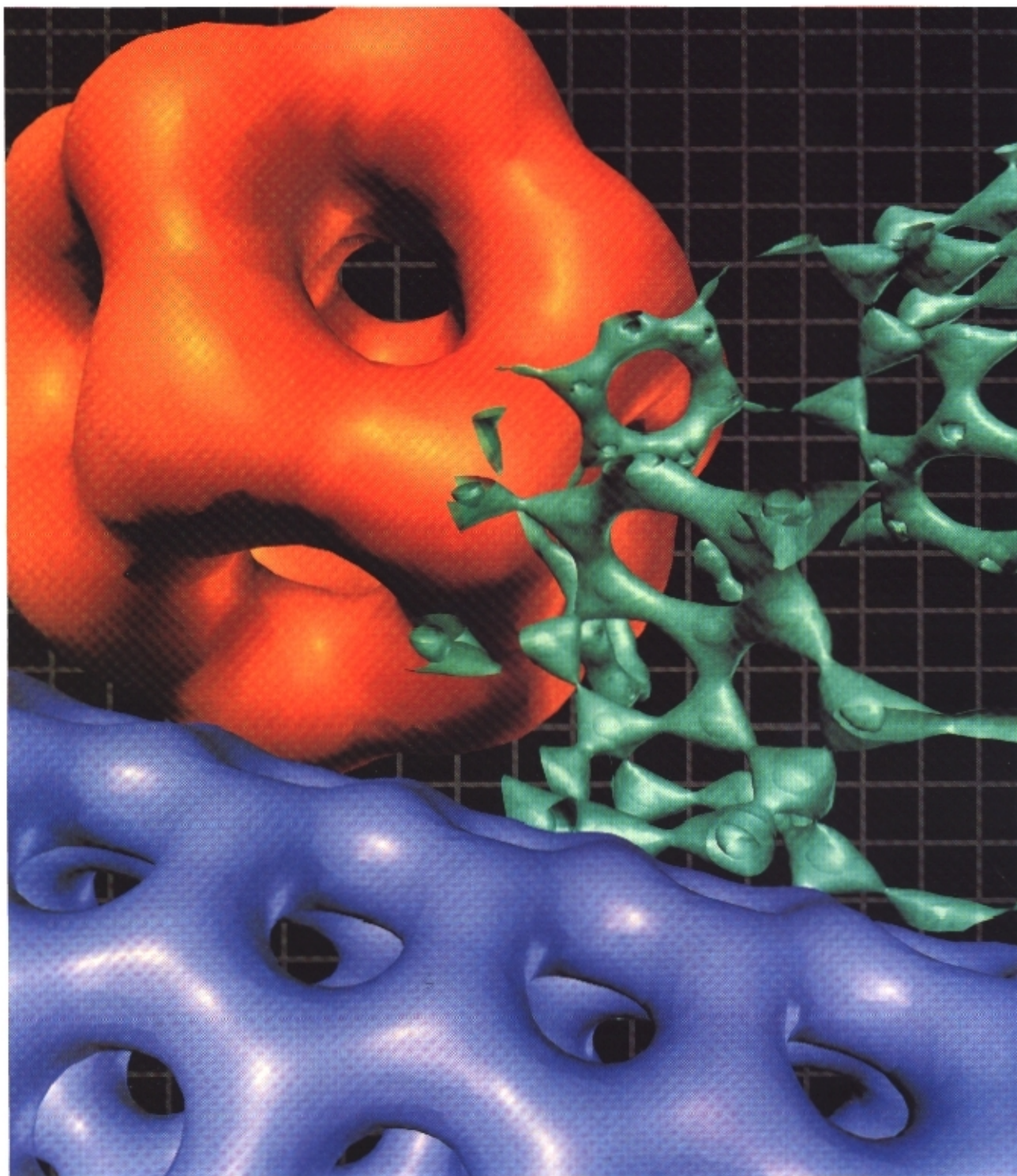


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COMPUTATIONAL MATERIALS SCIENCE

COMPUTATIONAL MATERIALS SCIENCE: THE ERA OF APPLIED QUANTUM MECHANICS

For many centuries, materials were discovered, mined, and processed in a largely serendipitous way. However, the characterization of the atom and the progress made in x-ray diffraction during the early years of this century started a quest for a theory of materials in terms of their atomic constituents. Later decades saw scientists developing many qualitative and semi-quantitative models that explained the principles of atomic cohesion and the basic properties of semiconductors, metals, and salts. Considering their simplicity, some of the models were surprisingly accurate and led to remarkable progress. However, for most materials of current interest, the interatomic interactions are intricate enough to require fairly elaborate models. Fortunately, we are entering an era in which high-performance computing is coming into its own, allowing true predictive simulations of complex materials to be made from information on their individual atoms.

Methods for computing the properties of materials can be divided into two classes: those that do not use any empirically or experimentally derived quantities, and those that do. The former are often called *ab initio*, or first-principles methods; while the latter are called empirical or semi-empirical. The *ab initio* methods are particularly useful in predicting the properties of new materials or new complex material structures, and for predicting trends across a wide range of materials. The semi-empirical methods excel at interpolating and extrapolating from known properties. This article focuses on the *ab initio* methods, which retain their predictive power even when experimental data are scarce or unavailable.

Methodology of *ab initio* calculations

As is well known, the binding in molecules and solids is due to the Coulomb forces between electrons and nuclei. The exact solution of the full, many-body Schrödinger equation describing a material is, of course, impossible, but one can make surprisingly accurate approximations of a system's ground state, and such approximations are widely used in condensed-matter physics. These approximations are based on density functional theory (DFT),¹ which was developed at the University of California, San Diego, by Walter Kohn, Pierre Hohenberg, and Lu Sham (and for which Kohn shared the 1998 Nobel Prize in chemistry with John Pople, a pioneer in quantum chem-

The properties of new and artificially structured materials can be predicted and explained entirely by computations, using atomic numbers as the only input.

Jerzy Bernholc

ψ_i , which satisfy the Schrödinger-like equations (in Rydbergs):

$$\left(-\nabla^2 + V_N(\mathbf{r}) + \int \frac{2\rho(\mathbf{r}')d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} + \mu_{xc}[\rho(\mathbf{r})] \right) \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}),$$

$i = 1, \dots, M.$

The first term represents the kinetic energy; the second is the potential due to all nuclei; the third is the classical electron-electron repulsion potential; and the fourth, the so-called exchange and correlation potential, accounts for the Pauli exclusion principle and spin effects. The exact form of the exchange-correlation term is unknown, but a *local* approximation, in which the exchange-correlation potential of a homogeneous electron gas of density $\rho(\mathbf{r})$ is used at each point, has proved highly successful. DFT generally predicts lattice constants, atomic positions, elastic properties and phonon frequencies with errors smaller than a few percent. For example, my research group at North Carolina State University computed the radial distribution function of the then new solid C₆₀ (see figure 1) six months before the first neutron scattering data, yet the result of the computation agreed almost perfectly with experiment.² In fact, the theoretical results were used for the initial calibration of the experimental setup.

Density functional theory predictions of cohesive energies used to be less accurate, but including terms dependent on the gradient of the electron density has substantially improved the agreement with experiment and with high-level quantum chemistry calculations.³

Large-scale computations

Because the electronic structure calculations described above are computationally demanding, progress in the field depends in perhaps equal measure on advances in theoretical methods and on advances in computer technology. For simple materials, such as silicon with only two atoms in a periodically repeated unit cell, the computational effort required has become so modest now that the calculations can be carried out on any contemporary personal computer. However, understanding the growth and properties of silicon devices requires calculating the characteristics of silicon surfaces. Because silicon is a covalently bonded material, the creation of a surface leads to

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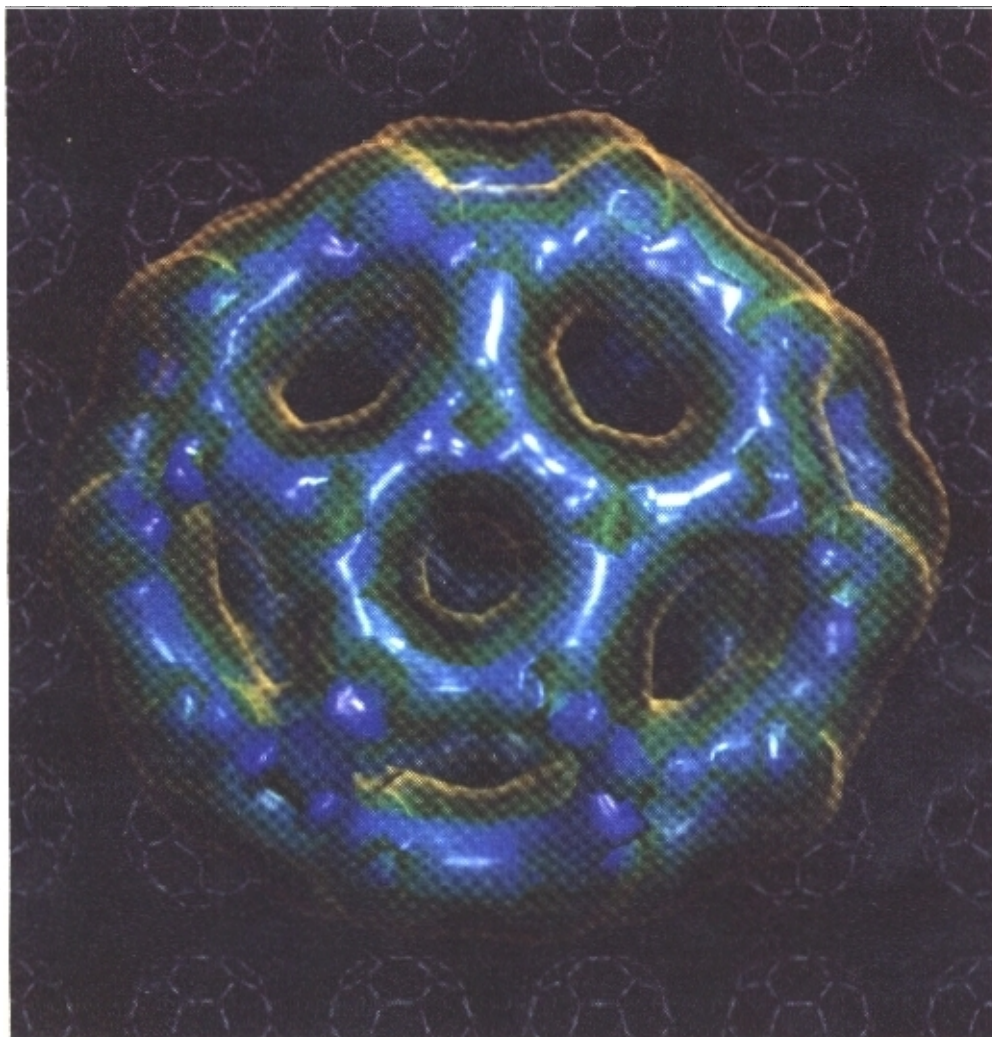


FIGURE 1. CALCULATED electron distribution in C_{60} at 1000 K, obtained from quantum molecular dynamics simulations.² Yellow, green, and blue denote regions of successively greater electron density. The atomic structure of C_{60} (background) consists of five- and six-membered rings arranged in the shape of a soccer ball.

broken bonds. This process is energetically unfavorable, so some atoms will move to rebond, forming a *reconstructed* surface with less symmetry. (See the article by John J. Boland and John H. Weaver, *PHYSICS TODAY*, August 1998, page 34.) Depending on the complexity of the resulting structure, the number of atoms N that one must consider in the unit cell will range from 16 to 400. Because the size of the computational effort grows roughly as N^2 , and asymptotically even as N^3 , it is no wonder that progress in computational materials physics is closely tied to progress in methodology and computers.

The largest *ab initio* calculations usually make use of functions called “pseudopotentials,” which replace the nuclear potential and the chemically inert core electrons with an effective potential, so that only valence electrons are explicitly included in the calculations. (See the article by Marvin L. Cohen, *PHYSICS TODAY*, July 1979, page 40; also see ref. 4.) The pseudopotentials are derived from atomic calculations that use atomic numbers as the only input. Because pseudo wavefunctions are smooth and nodeless, plane waves can be used as a basis set. This offers three major advantages:

- ▷ Plane waves do not depend on the atomic positions, so using them makes the results more precise.
- ▷ The accuracy of the result is determined by a single parameter, the highest kinetic energy of the waves included in the calculations.
- ▷ The kinetic energy ($-\nabla^2$) is diagonal in Fourier space, whereas the potential is diagonal in real space.

The transformation between the two spaces occurs via

dynamics for the atoms.⁵ Another approach is to solve iteratively for the electronic wavefunctions, compute the forces, and move the atoms by a large step.⁶ In both cases the atoms follow Newton’s equations of motion with *ab initio* interatomic forces. These methods are called *ab initio*, or quantum molecular, dynamics.

Ab initio calculations have long been useful in explaining experimental results and providing unique insights. The recent advances make it possible to predict the properties of materials with complex atomic arrangements, whose study would have been prohibitively expensive just a few years ago. The examples below illustrate the role that accurate and quantitatively reliable calculations can play in modern condensed matter physics and materials science, while also highlighting the advantages of collaboration and close interaction between theorists and experimenters.

Solid C_{36}

Some of the most exciting new materials discovered in the last decade are the fullerenes. Solid C_{60} , once it was produced in quantity, was shown to have a number of remarkable properties, including superconductivity after intercalation with alkali metal atoms. In fact, its transition temperatures T_c are approaching 40 K, second only to high- T_c oxides. The relatively high T_c of C_{60} is due to the strong electron-phonon interaction in curved fullerenes. This has stimulated Marvin Cohen, Steven Louie, and their coworkers at the University of California, Berkeley, to examine fullerenes with even greater curvatures.⁷ In-

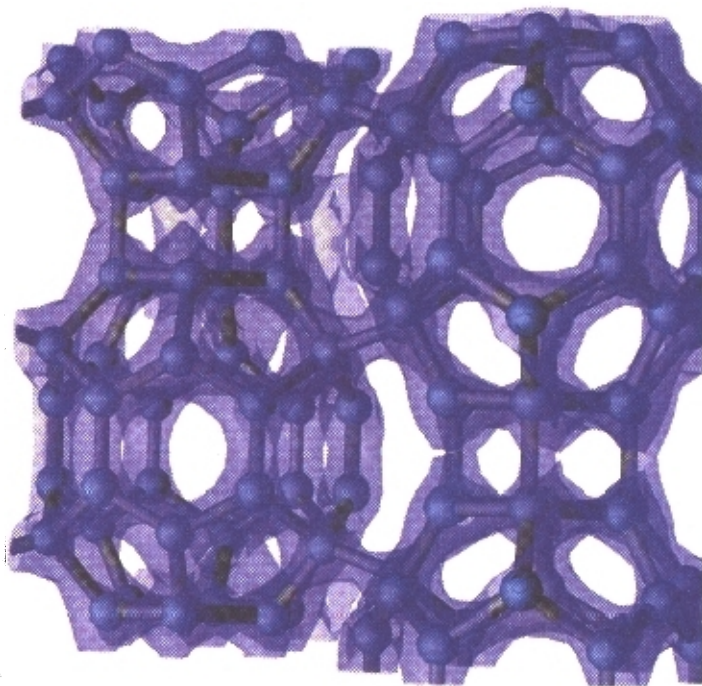


FIGURE 2. ATOMIC STRUCTURE and surface of constant charge density of rhombohedral C_{36} . Blue spheres represent carbon atoms. The covalent-like bonding between the C_{36} units is clearly visible. It is predicted that this new solid will form from individual molecules and will exhibit high-temperature superconductivity. (From ref. 7.)

deed, they showed that a solid formed out of C_{36} should have even more remarkable properties. Unlike the molecules in the C_{60} solid, the individual C_{36} molecules crosslink (see figure 2). The cohesive energy of solid C_{36} should be comparable to that of solid C_{60} , and the density of electronic states at the Fermi level should also be high, as is necessary for high T_c according to the Bardeen-Cooper-Schrieffer theory of superconductivity. And the electron-phonon coupling? The calculations show that it is even stronger than in C_{60} , so that solid C_{36} is an excellent candidate for a superconducting solid with a high T_c .

How about an experimental confirmation? Growing a "designer" solid is not easy. The C_{36} molecules form in the gas phase, but Alex Seattle's group (also at Berkeley) was able to deposit them on a substrate and measure some of their properties. Indeed, the individual molecules turn out to be more reactive than C_{60} molecules and seem to form dimers and trimers. But a solid sample of C_{36} good enough for the delicate measurements of superconducting behavior remains to be made.

Silicon

Let us now turn to the technologically important case of silicon. Although most physicists think of devices as being made of a single crystal, polycrystalline silicon is used extensively in microelectronics. When polycrystalline silicon is doped, a significant number of dopant atoms segregate to the grain boundaries and become electrically inactive. What are the driving forces for that behavior, and can it be prevented?

Consider the case of a substitutional donor, arsenic. Experiments indicate that its segregation energy is substantial, about 0.5 eV. How is that possible? We know from elementary chemistry that arsenic has the propensity to be either trivalent or pentavalent. It is the perfection of crystalline silicon that forces it to assume a four-fold coordination and thus become a shallow donor. However,

at a grain boundary the coordination constraint becomes weaker. There is more room for relaxation, and arsenic atoms can assume their preferred three-fold coordination. Wouldn't that behavior break bonds and make some silicon atoms very unhappy? Not if arsenic atoms act in *pairs*, effectively breaking one bond and moving away from each other. Indeed, calculations by a joint theoretical-experimental team headed by Sokrates Pantelides of Vanderbilt University and Stephen Pennycook of Oak Ridge National Laboratory found dimers and even chains of dimers to be energetically favorable.⁸ In fact, dimer chains, shown in figure 3, were somewhat preferred.

The story does not end there. Two years later the same team succeeded in imaging the arsenic atoms at a grain boundary, albeit a more complex boundary than the one examined theoretically. Arsenic atoms were indeed in the dimer configurations, but the dimers were isolated. Follow-up calculations, although carried out for an idealized system, provided the explanation in terms of kinetic constraints, the atomic geometry at the more complex boundary, and entropic effects at the fairly high doping temperature.

Magnetism

In the early days of quantum mechanics, the Heisenberg and Ising models of magnetism provided important conceptual models for the entire field of phase transitions. However, magnetic phenomena are complex, and there are still many unsolved problems—especially at the microscopic level—because spin effects are so subtle. Harnessing magnetic phenomena to the fullest extent possible is also important for many applications, most notably in high-density computer storage.

In DFT it has long been possible to carry out spin-polarized calculations, treating the spin-up and spin-down electrons separately. For largely homogeneous systems, where there is a single preferred spin direction, that treatment has worked well and has led to a number of surprises. It is now well accepted that magnetism is an effect of *undercoordination*, in which some atoms have fewer neighbors than the maximum number of bonds they can form. This is because in a covalent bond a spin-up electron pairs up with a spin-down electron, leading to no net spin. Nevertheless, it took years to arrive at a satisfactory description of low-coordinated systems. Pioneering calculations by Arthur Freeman and his coworkers at Northwestern University have shown that surface layers can possess magnetic moments enhanced far beyond those in the bulk, and that thin films of nonmagnetic metals can become magnetic.

In disordered or low-symmetry systems, even more complicated spin arrangements are possible, in which the various spins are not aligned along a single preferred direction. How do we know which arrangement is energetically favored? The usual procedure is to compute the energies of each competing structure to identify the ground state. This can be tedious. But there is a better way. Ulf von Barth and Lars Hedin at the University of Lund devised a generalized spin-density theory in which the wavefunctions are two-component spinors $\Psi(\mathbf{r}) = [\psi_1(\mathbf{r}), \psi_2(\mathbf{r})]$, where ψ_1 and ψ_2 are complex functions. This approach allows the spin quantization axis to vary continuously with position, but the total energy needs to be minimized without any constraints on the spin direction. Very recently, Car and his coworkers at the Institute for Numerical Research in Lausanne, developed a generali-

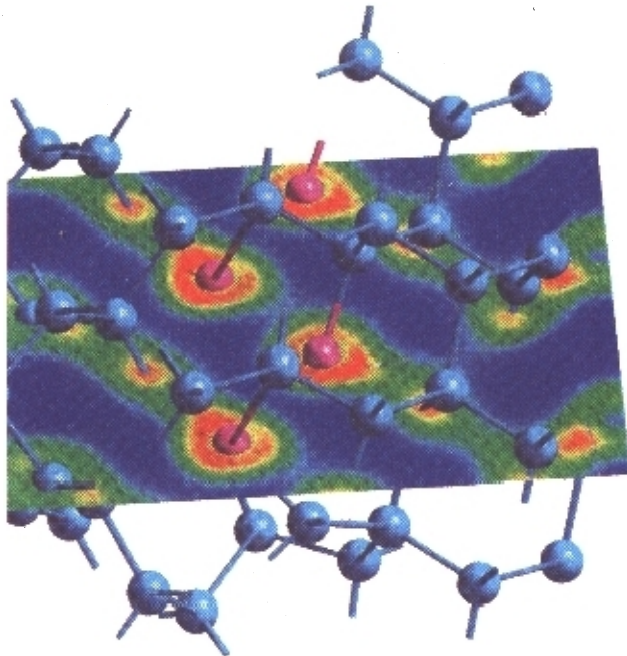


FIGURE 3. GRAIN BOUNDARY. This two-dimensional plot shows the electron density at a silicon grain boundary saturated by a chain of arsenic atoms. The arsenic atoms are shown in red, the silicon atoms in blue. The color scheme (in order of decreasing electron density) is red, yellow, green, light blue, and deep blue. (From ref. 8.)

zation of the Car–Parrinello procedure that simultaneously optimizes both the spin directions and the atomic coordinates.⁹ The first applications to small iron structures found both collinear and noncollinear ground states, depending on the cluster size. (See figure 4.) Very interestingly, there are energy barriers separating the collinear and noncollinear structures. Such barriers do not exist in the classical Heisenberg model of a spin system.

This example also highlights the emergence of clusters as a new and exciting class of materials. Atoms in clusters are undercoordinated compared to those in bulk, resulting in different structures, larger magnetic moments, and enhanced reactivity patterns in catalysis. Clusters may become the building blocks of a host of new materials, but their structures and properties, which can vary dramatically with cluster size, must first be well understood.

New methods

Although materials computations have already advanced quite far, the quest for faster and bigger calculations continues unabated. This has stimulated interest in “real space” methods, which avoid the use of plane waves that extend throughout the entire system by having the vast majority of operations be local, in “real space.” Working

in real space has several advantages. It allows one to use advanced mathematical techniques that automatically separate the various length scales present in the problem, substantially accelerating convergence. (See the box below.) Also, parallelization becomes much easier, because each processor can be assigned a given region of space. Finally, real-space methods may reduce scaling of the computational effort with system size to the order of the number of atoms N rather than the current $O(N^3)$.

The easiest way to exploit the multiscale aspects of real-space calculations is by using methods based on techniques of applied mathematics: multigrids, wavelets, and finite elements. Of those three, the grid-based methods¹⁰ have progressed the most in applications, and I will give a few examples here.

For clusters, grid-based methods offer a natural advantage by making it easy to implement boundary conditions. James Chelikowsky and his group at the University of Minnesota have beautifully exploited that advantage in determining structural properties, polarizabilities, optical energy gaps, and excitation spectra.¹¹ It is much easier to calculate optical gaps in clusters than in the bulk, because in clusters even corrections to density functional theory can be determined by computing the DFT total energy differences. Excitation spectra are significantly more difficult to work with, but again the real-space methodology and the small size of the clusters allow simplification. Using expressions derived from time-dependent local density theory, Chelikowsky and his colleagues obtained excellent results for the spectra and polarizabilities of sodium and silicon clusters. The agreement with experiment was almost as good as in high-quality quantum chemistry calculations, which are much more expensive to do.

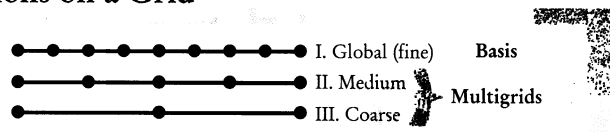
There have also been a substantial number of large-scale solid-state applications of real-space methods. In my own group, the multigrid approach is now the method of choice for studies of large systems. We have used it to determine large surface reconstructions and their optical spectra, and to investigate doping, surface melting, and

Multiscale Calculations on a Grid

Multiscale phenomena occur in many areas of physics. In each case we can use the same conceptual framework: Consider an iterative solution of a differential equation on a grid. Although the iterations quickly reduce error components that are oscillatory on the scale of the grid, the long-wavelength components converge only slowly. However, the approximate solution can be transferred to a coarsened grid, where the error is now oscillatory, and iterated there. After a convergence slowdown is observed, a still coarser grid is used.

Up to this point, the coarsening procedure is very reminiscent of the renormalization-group approach, which focuses on the large-scale features of the problem. However, in the *multigrid* method, developed by the mathematician Achi Brandt of the Weizmann Institute, one recursively transfers the coarse-grid solutions back to finer grids.¹⁸ This introduces high-frequency errors, of course, but they are easily removed by a few iterations. Thus we obtain a machine-precision solution in $O(K)$ operations, where K is the number of points on the fine grid.

Actual calculations require high accuracy and thus high-or-



der discretizations, because the cohesive energy is a very small fraction of the ground-state energy. Consider, as an example, the one-dimensional Poisson equation, $\Phi''(x) = f(x)$. By Taylor-expanding $\Phi(x)$, we obtain an approximate discretization based on central finite differences:

$$[\Phi(x_i - h) - 2\Phi(x_i) + \Phi(x_i + h)]/h^2 = f(x_i) + O(h^2).$$

However, expanding both $\Phi(x)$ and $f(x)$, and using the fact that $\Phi''(x)$ is equal to $f(x)$ at convergence, leads to a more accurate expression that still involves only the nearest neighbors:

$$\begin{aligned} [12\Phi(x_i - h) - 24\Phi(x_i) + 12\Phi(x_i + h)]/h^2 \\ = f(x_i - h) + 10f(x_i) + f(x_i + h) + O(h^4). \end{aligned}$$

The short range of this “Mehrstellen” discretization is particularly important for parallelization and $O(N)$ methods.

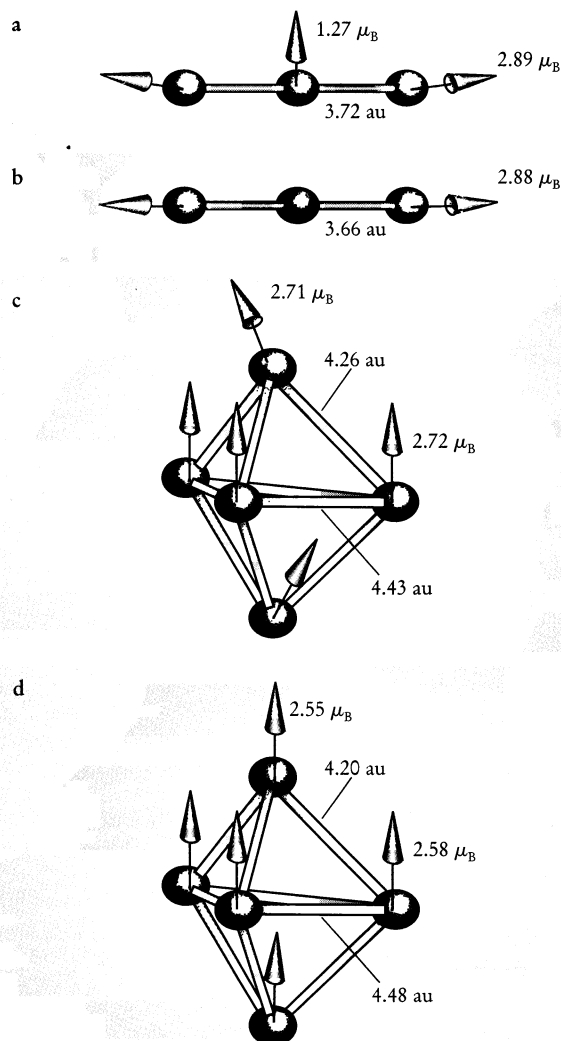


FIGURE 4. ATOMIC AND MAGNETIC STRUCTURES of Fe_3 and Fe_5 clusters. In the isomers a and c the spins are noncollinear. The corresponding collinear structures are b and d. Magnetic moments are often much larger in clusters than in bulk, a fact that could be important for applications. (From ref. 9.)

material to date, and there will be no shortage of exciting applications when nanotubes can be grown in sufficient quantity and quality.

Overcoming size limits

We now turn to methods that seek to overcome the limits on the size of the systems that can be studied *ab initio*. There is an urgent, growing need to include more and more atoms in simulations—new space-age materials are becoming more complex or consist of multiple layers of “simple” materials that have to be modeled together.

Computer designers are doing their part, but the standard density functional methods described above present a problem. Consider a system of N atoms. As N grows, the number of electrons it contains grows as $O(N)$. In a solid, the wavefunction of each electron can extend over the whole solid, which means that computing one wavefunction will take at least $O(N)$ operations. Hence, the computations must scale at least as $O(N^2)$. Furthermore, the individual wavefunctions must be orthogonal to each other, and the process of orthogonalization or diagonalization scales as $O(N^3)$.

Recently, a number of ingenious methods have been proposed for evaluating the ground-state energy in $O(N)$ operations. How is that possible? The main idea in most of the approaches is to use a basis of *localized*, variationally optimized functions. Each function is confined to a given region of space, but the various confinement regions overlap so that there is little loss of generality. Because the matrix elements between functions localized in regions sufficiently far away will vanish, the number of non-zero elements becomes $O(N)$. Nevertheless, the results are still quite accurate with only a few functions per atom and with localization regions spanning only a few bond lengths. Recent reviews have compared the various aspects of the proposed $O(N)$ methods.¹³

The DFT-based $O(N)$ methods are still being developed, but the localized functions are turning out to be useful even apart from facilitating very-large-scale calculations.¹⁴ The optimization shown in figure 5, for example, which was started from random numbers, led to a chemically very intuitive result: a function strongly localized on a carbon-carbon bond. That example provides some insight into and justification for expecting the eventual success of $O(N)$ -like methods.

Chemists have long known that good approximations of the cohesive energies of complicated structures can often be obtained by summing up the known “strengths” of the individual bonds. Using the quantum-mechanical basis functions that automatically localize in bonding regions should lead to accurate results while keeping the number of basis functions to a minimum. The strict localization also makes it more efficient to do large-scale parallelization, and it is likely that DFT calculations including more than a thousand atoms will appear soon. Such calculations should have a significant impact on our understanding of complicated solids, large biomolecules, and complex liquids.

Beyond density functional theory

Density functional theory has known drawbacks. For example, it does not do well in describing properties that involve excited states, such as bandgaps of semiconductors and insulators. That limitation is not surprising though,

nanotubes. Quantum molecular dynamics, which must conserve total energy to a high degree of accuracy, works very well and allows for large time steps. The advantage of multigrids becomes particularly apparent in systems where convergence is difficult to attain because of such obstacles as charge sloshing or multiple length scales. The use of parallelization has also been very effective in our work, and the computational speed on the massively parallel Cray T3E computer has scaled linearly with the number of processors—up to 1024, the maximum number to which we had access.

As an example of a specific application, consider nanotubes, which are the strongest materials known. Early classical molecular dynamics simulations indicated that they had exceptional strength, a suggestion that needed to be confirmed. However, because currently made nanotubes are so very short, it is extremely difficult to measure their strengths. With no experimental data available at the time, *ab initio* simulations to determine the mechanisms of breakage seemed to be the next best approach. But how were they to be performed, if even the classical simulations had proved computationally expensive? Well, there was a trick—namely, to simulate a tube at a high fixed dilation and high temperature. Indeed, a long quantum molecular dynamics computer run identified the key transformation that leads to either breakage or plastic behavior, depending on the temperature and strain rate.¹² The predicted strength is the highest by far of any

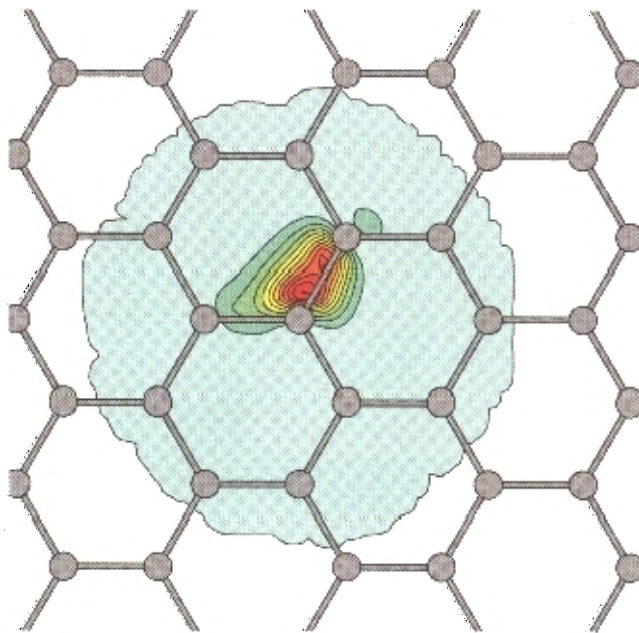


FIGURE 5. OPTIMIZED ELECTRON-DENSITY FUNCTION for a carbon nanotube, calculated by Jean-Luc Fattebert and his coworkers at North Carolina State University. Note that although the allowed localization region extends over 6 Å (shaded in blue), this function is largely confined to one carbon-carbon bond. The plotting plane is along the surface of the nanotube. The calculations used a non-orthogonal orbital multigrid generalization of a method proposed by Giulia Galli and Michele Parrinello. The optimized localized functions have already enabled Fattebert and Marco Buongiorno Nardelli to make efficient *ab initio* calculations of quantum transport in nanotubes.

because DFT is a variational approach for obtaining the total energy of only the *ground state*. To obtain the energies of the excited states, we need to use many-body theory and properly take into account the nonlocal interaction between electrons. The simplest working theory, the so-called GW approximation, developed by Hedin and adapted for use with semiconductors by Steven Louie and Mark Hybertsen,¹⁵ leads to bandgaps in excellent agreement with experiment.¹⁶ However, the computational expense is significantly greater than that of DFT calculations, and further simplifications would be desirable.

Although the DFT ground-state energies, and in particular the *differences* between the energies of alternative ground-state structures, are quite accurate, the errors in unfavorable cases are often still too large, because the exchange-correlation potential is not known exactly. If greater accuracy is required, a sophisticated many-body treatment is again necessary. The most successful methodology is based on the quantum Monte Carlo approach, in which the full many-electron equations are solved by statistical sampling.¹⁷ Although it is substantially more expensive than density functional theory, the quantum Monte Carlo approach is likely to be the method of choice for high-accuracy benchmark calculations in small and medium-sized systems.

Future outlook

Progress in materials simulation is accelerating while also becoming more important. The rapid increase in the speed of computers is likely to continue unabated for at least the next decade, and possibly significantly longer. The algorithmic progress, stimulated by the interest and advances in the field, is even more robust. As some of the examples above illustrate, it is already possible to predict many properties reliably, and in some cases the theoretical input has stimulated important experimental discoveries. As the capabilities for performing realistic simulations increase, it might become possible to routinely "design" on a computer, at least in part, a new material with desirable properties. The candidate materials would be examined theoretically and only the most promising ones would be investigated experimentally.

Materials growth and processing is another field that would benefit significantly from reliable simulations. Although the industrially relevant processes are often rather

complicated, materials simulations are coming to be recognized as an important component of industrial R&D. Atomistic-simulation software is being marketed to industry, and major industrial firms such as Motorola and Dow Chemical are building up their materials-theory departments. The US government, which has long been the driving force in high-performance computing, has made materials simulation one of its main areas of emphasis. In view of the current interest in it and its rate of progress, the field of materials simulation is likely to experience rapid growth and a commensurate expansion in job opportunities.

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References

1. P. Hohenberg, W. Kohn, *Phys. Rev.* **136**, B864 (1964). W. Kohn, L. Sham, *Phys. Rev.* **140**, A1133 (1965). R. M. Dreizler, E. K. U. Gross, *Density Functional Theory*, Springer, Berlin (1990).
2. Q.-M. Zhang, J.-Y. Yi, J. Bernholc, *Phys. Rev. Lett.* **66**, 2633 (1991). R. L. Cappelletti, J. R. D. Copley, W. A. Kamitakahara, F. Li, J. S. Lannin, D. Ramage, *Phys. Rev. Lett.* **66**, 3261 (1991).
3. J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, C. Fiolhais, *Phys. Rev. B* **46**, 6671 (1981).
4. D. R. Hamann, M. Schluter, C. Chiang, *Phys. Rev. Lett.* **43**, 1494 (1979).
5. R. Car, M. Parrinello, *Phys. Rev. Lett.* **55**, 2471 (1985).
6. M. C. Payne, D. C. Allan, M. P. Teter, T. A. Arias, J. D. Joannopoulos, *Rev. Mod. Phys.* **64**, 1045 (1992).
7. M. Côté, J. C. Grossman, M. L. Cohen, S. G. Louie, *Phys. Rev. Lett.* **81**, 697 (1998).
8. A. Maiti, M. F. Chisholm, S. J. Pennycook, S. T. Pantelides, *Phys. Rev. Lett.* **77**, 1306 (1996). M. F. Chisholm, A. Maiti, S. J. Pennycook, S. T. Pantelides, *Phys. Rev. Lett.* **81**, 132 (1998).
9. T. Oda, A. Pasquarello, R. Car, *Phys. Rev. Lett.* **80**, 3622 (1998).
10. E. L. Briggs, D. J. Sullivan, J. Bernholc, *Phys. Rev. B* **52**, R5471 (1995). J. R. Chelikowsky, N. Troullier, Y. Saad, *Phys. Rev. Lett.* **72**, 1240 (1994). F. Gygi, G. Galli, *Phys. Rev. B* **52**, R2229 (1995). K. A. Iyer, M. P. Merrick, T. L. Beck, *J. Chem. Phys.* **103**, 227 (1995). G. Zumbach, N. A. Modine, E. Kaxiras, *Solid State Comm.* **99**, 57 (1996).
11. I. Vasiliev, S. Ögüt, J. R. Chelikowsky, *Phys. Rev. Lett.* **82**, 1919 (1999).
12. M. Buongiorno Nardelli, B. I. Yakobson, J. Bernholc, *Phys. Rev. B* **57**, R4277 (1998).
13. G. Galli, *Current Opinion in Solid State & Materials Science* **1**, 864 (1996). P. Ordejon, D. A. Drabold, R. M. Martin, M. P. Grumbach, *Phys. Rev. B* **51**, 1456 (1995).
14. N. Marzari, D. Vanderbilt, *Phys. Rev. B* **56**, 12847 (1999).
15. L. Hedin, *Phys. Rev.* **139**, A796 (1965). M. S. Hybertsen, S. G. Louie, *Phys. Rev. B* **34**, 5390 (1986).
16. F. Aryasetiawan, O. Gunnarsson, *Rep. Prog. Phys.* **61**, 237 (1998).
17. D. M. Ceperley, L. Mitás, *Adv. Chem. Phys.* **93**, 1 (1996).
18. W. L. Briggs, *A Multigrid Tutorial*, SIAM Books, Philadelphia (1987). A. Brandt, *Math. Comp.* **31**, 333 (1977). A. Brandt, *GMD Studien* **85**, 1 (1984). ■